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**September 2007 RCRA Consent Decree Progress Report**

**CDM Status Update on Bench-Scale  
PRB Testing Work Plan - September 2007**



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## **Memorandum**

**To:** *Bob Miller and Jon Nickel, Asarco*

**From:** *Angela Frandsen and Bob Kimball, CDM*

**Date:** *September 21, 2007*

**Subject:** *East Helena PRB Materials Testing – Jar Test Results*

### **Introduction**

CDM has completed the jar testing (Phase I) evaluation of candidate in-situ treatment media for potential suitability as Permeable Reactive Barrier (PRB) materials for removing arsenic contamination in groundwater at the East Helena smelter.

Presently, the predominant environmental concern associated with the smelter site is the arsenic contamination emanating from the site in the intermediate aquifer. CDM has previously evaluated pump and treat technology at the site to address the arsenic contamination. However, Asarco also desires to determine the suitability of in-situ treatment using permeable reactive barriers.

The original scope of work envisioned the evaluation of potential in-situ groundwater treatment/arsenic removal options being conducted in a phased approach, as follows:

- **Phase I. Jar Testing:** Phase I consists of testing various media under various batch conditions to determine the different media's capacity to remove/remediate arsenic.
- **Phase II. Column Testing:** Phase II testing will be performed on selected media, based upon the results from Phase I testing. Column testing provides test conditions that are more representative of the actual site conditions. Data obtained from Phase II testing will provide the necessary data for preliminary system design.
- **Phase III. Pilot-scale Testing:** In-situ pilot-scale testing may be conducted, depending on the results of the previous two phases and input from Asarco. This determination will likely be made based on the certainty of performance and cost of the full-scale system based on column test results.

This memorandum summarizes the results of the Phase I Jar Testing conducted in June and August 2007.

## Jar Testing Procedure

Jar tests were conducted on various media to determine their adsorptive capacity for arsenic from the site groundwater. Jar testing was conducted in June 2007 with follow-up testing conducted in August 2007.

Groundwater from Well DH-17 (near the existing EPA zero valent iron PRB pilot test) was used in the jar testing. Water quality data for this well ("feed water" data) are summarized in Table 1. The sample was submitted to the laboratory for the full suite of parameters suggested in the May 16, 2007 EPA comments. Dissolved silica and phosphorous were added to the analyte list because these can interfere/compete with arsenic for adsorption sites. Arsenic concentrations are near 40 milligrams per liter (mg/L) with arsenic speciation indicating 100 percent as the reduced form of arsenic (+3).

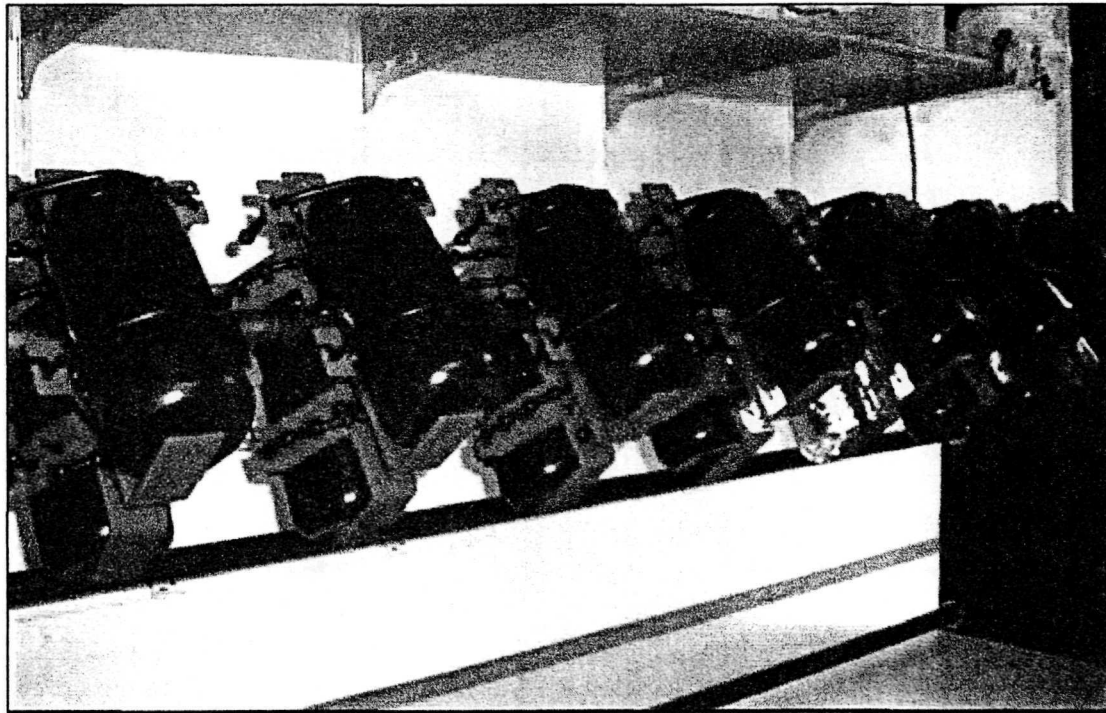
**Table 1**  
**Well DH-17 Water Quality, June 19, 2007**

<b>Metals:</b>			<b>Other Parameters</b>	
(all in mg/L)	<b>Dissolved</b>	<b>Total Recoverable</b>	(units as noted)	
Aluminum	0.1 U	0.1 U	Total Suspended Solids, mg/L	10 U
Antimony	0.005 U	0.005 U	Total Dissolved Solids, mg/L	1,680
Arsenic	36.84	40.6	Sulfate, mg/L	739
Barium	0.1 U	0.1 U	Total Alkalinity as CaCO <sub>3</sub> , mg/L	450
Beryllium	0.001 U	0.001 U	Bicarbonate as HCO <sub>3</sub> , mg/L	550
Cadmium	0.001 U	0.001 U	Chloride, mg/L	50
Calcium	29	30	Total Phosphorous, mg/L	1.05
Chromium	0.01 U	0.01 U	Total Organic Carbon, mg/L	3.8
Cobalt	0.01 U	0.01 U	pH	7.18
Copper	0.01 U	0.01 U	Specific Conductivity (mS/cm)	2.43
Iron	0.57	0.63	Eh (mV)	+121
Lead	0.01 U	0.01 U	Temperature (C)	13.7
Magnesium	9	9	<b>Speciation</b>	
Manganese	1.39	1.43	Arsenic-III, mg/L	37
Mercury	0.001	0.001 U	Arsenic-V, mg/L	0.1 U
Nickel	0.01 U	0.01 U	Selenium-IV, mg/L	0.005 U
Potassium	10	11	Selenium-VI, mg/L	0.001 U
Selenium	0.005 U	0.005 U		
Silica	14.7	15.7		
Silver	0.005 U	0.005 U		
Sodium	580	621		
Thallium	0.005 U	0.005 U		
Tin	0.1 U	0.1 U		
Vanadium	0.1 U	0.1 U		
Zinc	0.17	0.17		

In general, the jar test procedure consisted of:

- Collecting a feed water sample for raw water quality analysis.
- Adding water to jars filled with varying quantities of media. Jars were completely filled with no headspace to minimize the potential for exposing the sample to the atmosphere (except for the "no media" jar). Amber jars or aluminum foil wrap were used to block the light and minimize the potential for photo-oxidation of the arsenic.
- Agitating the jars overnight (approximately 24 hours) using a rotary tumbler.
- Opening the jars and collecting and collecting filtered samples (no total metals analysis) from each jar and submitting them to the laboratory for analysis.
- Collecting field measurements for pH, ORP, conductivity and temperature on the remaining solution.

Figure 1 shows the jar tumbler apparatus that was used to shake the jars overnight.



**Figure 1. Jar tumbler apparatus and jars.**

***Media Preparation***

The media that were used in the jar tests were as follows:

- Zero Valent Iron (ZVI - remaining onsite from EPA PRB test)
- Unfumed Slag (Iron-bearing slag from Asarco East Helena smelter)
- Taconite Concentrate (U.S. Steel - iron-rich sand material used in their process)
- Taconite Tailings (U.S. Steel - waste material)
- Taconite Pellet Fines (U.S. Steel - iron rich material left over from manufacture of taconite pellets - compressed taconite concentrate)
- Granular Ferric Hydroxide (GFH - Siemens/US Filter)
- Bayoxide E33 (Severn Trent - a ferric hydroxide material)
- Bauxsol "Klosur" (Virotech - Bauxsol [byproduct of the aluminum refining industry] with oxidant additive)
- Bauxsol "Proactive" (Virotech - Bauxsol without an oxidant additive)
- Dow Adsorbsia (Dow Chemical - titanium-based arsenic adsorption media)
- Silica sand (control)
- Manganese dioxide slag (waste material from historic Butte Reduction Works in Butte, MT, used to test oxidation of As +3 to As +5)
- Manganese dioxide (Erachem - commercial grade product called "EMD", used to test oxidation of As +3 to As +5)

The ZVI, GFH, Bayoxide, Dow Adsorbsia, Taconite pellet fines, Erachem manganese dioxide, and silica sand were tested "as is" without sieving as they were already granular. The Taconite concentrate and tailings materials ranged from powder to coarse gravel and were sieved to obtain the sand size fraction (minus 2 millimeter but greater than 0.6 millimeter). The fines and coarse grains were not used. The unfumed slag and manganese dioxide slag were ground by hand and similarly sieved to obtain the sand size fraction.

The exceptions to this sieving protocol were the two Bauxsol reagents from Virotech which were provided by the vendor as powders (Bauxsol has been used for source control by slurry injection). Because there was no sand size fraction, the Virotech Bauxsol materials were tested as provided. The powdered form increases the surface area and adsorptive capacity. This factor was considered in the analysis of the adsorption test results.

CDM Helena was able to borrow a portable voltammetric analyzer (PDV 6000 Portable Heavy Metals Analyzer) from the CDM Denver office for use in screening arsenic concentrations during the jar test. The instrument was used to obtain screening-level arsenic concentrations from initial testing to adjust the dosages of the different PRB media in subsequent tests to obtain better adsorption isotherms.

Prior to running the jar tests, a "dry run" was conducted to test the bottle-filling technique to minimize any potential oxidation from contact with the air and to test some initial dosages of PRB media (analysis using the portable arsenic field meter). With some trial and error, it was determined that 1) filling the jars slowly from the bottom, 2) capping the jars under water (to ensure no headspace) and 3) wrapping the lid with electrical tape to prevent leaks were adequate measures for maintaining anoxic conditions in the jars.

The results of the "dry run" indicated:

- 1) the jar filling method described above maintained the reducing conditions of the water
- 2) the initial dosages of taconite concentrate, slag, and ZVI (1 g/L, 5g/L and 10 g/L) were too small to significantly affect the arsenic concentration (based on the field instrument reading accuracy) and that larger dosages would be needed.

### **Summary of Jar Test Media and Dosages**

The first round of jar testing was conducted over three days (two nights) June 19 through 21. For the first test, 14 jars were setup with the intent of trying relatively "high" doses of PRB materials to determine whether or not the material affected arsenic concentrations. On the second day, these jars were opened and arsenic concentrations determined by the portable arsenic meter. These "field arsenic" readings provided guidance for media dosages for the second day of testing and also indicated which media simply did not work and did not require further testing.

A second set of jar tests was conducted on August 20, 2007 to test some additional media for arsenic adsorption and to test the effectiveness of manganese dioxide as a potential oxidant for the arsenic. The manganese dioxide was tested after noting good arsenic adsorption results on the Bauxsol Klosur media, which has an oxidant added, while poor arsenic adsorption results were noted on the Bauxsol Proactive media, which has no oxidant added. The solid manganese dioxide could potentially be a component of a PRB wall to oxidize the arsenic and thus increase adsorption capacity. A combination of manganese dioxide and taconite pellet fines was also tested to see if arsenic oxidation improved adsorption.

Table 2 summarizes the media and dosages tested for all of the jar testing done during the summer of 2007.

**Table 2**  
**Summary of Jar Test Media and Dosages**

Jar #	Media	Media Dose (g)	Field Arsenic (mg/L)	Sample sent to Lab?
<b>Round 1 (June 2007), Days 1 and 2</b>				
1	none - oxidation	NA	37.08	Y
2	ZVI	400	<0.16	Y
3	Unfumed Slag	200	30.4	Y
4	ZVI	100	0.539	Y
5	Taconite (concentrate)	200	29.52	Y
6	GFH	25	<0.16	Y
7	GFH	10	<0.16	Y
8	Bayoxide	25	<0.16	Y
9	Bauxol Klosur (w/oxidant)	10	0.436	Y
10	Bauxol Klosur (w/oxidant)	1	26.96	Y
11	Silica Sand	400	31.12	Y
12	Bauxol Proactive (no oxidant)	20	30.8	N
13	Bauxol Proactive (no oxidant)	10	32.72	N
14	Taconite tailings	300	31.44	Y
15	Bayoxide	0.5	--	Y
16	Bayoxide	1	--	Y
17	Bayoxide	5	--	N
18	Bayoxide	10	--	Y
19	GFH	0.5	--	Y
20	GFH	1	--	Y
21	GFH	5	--	N
22	Bauxol Klosur	0.5	--	Y
23	Bauxol Klosur	3	--	N
24	Bauxol Klosur	5	--	Y
25	ZVI	25	--	Y
26	ZVI	50	--	Y
27	Unfumed Slag	400	--	Y
28	Taconite (concentrate)	50	--	Y
<b>Round 2 (August 2007)</b>				
1	Taconite pellet fines	200.2	--	Y
2	Taconite pellet fines	75.1	--	Y
3	Taconite pellet fines	25	--	Y
4	Dow Adsorbsia	20	--	Y
5	Dow Adsorbsia	5.1	--	Y, sp
6	Dow Adsorbsia	1	--	Y
7	Butte MnO <sub>2</sub>	67.3	--	Y, sp
8	Butte MnO <sub>2</sub>	20.1	--	Y, sp
9	Erachem MnO <sub>2</sub>	24.9	--	Y, sp
10	Erachem MnO <sub>2</sub>	6.1	--	Y, sp
11	Taconite pellet fines + Erachem MnO <sub>2</sub>	25g tac + 6.1g MnO <sub>2</sub>	--	Y, sp

**Notes:**

"Field Arsenic" concentrations from the portable arsenic meter and are not analytical laboratory concentrations  
"Y, sp" indicates the sample was analyzed for arsenic speciation in addition to dissolved arsenic analysis

The portable arsenic meter was not used to analyze any of the jar samples from day 2 in June or during the second round of testing in August.

For the June testing, filtered samples were submitted to the laboratory for the following analytes: Ca, Mg, Na, K, As, Cd, Cu, Fe, Mn, Pb, Se, Zn, Al, Sb, Ba, Be, Cr, Co, Hg, Ni, Ag, Tl, Sn, Si, and V. The analyte list was expanded per EPA's May 16, 2007 comments and EPA's subsequent June 13, 2007 approval letter. Dissolved silica was added to check for potential interferences, as noted above. For the August testing, filtered samples were submitted for dissolved arsenic only or dissolved arsenic plus a few key analytes, depending on the media. Samples from the manganese dioxide oxidation tests were also submitted for arsenic speciation.

Because the original scope of work contained an allotment of 22 samples from the jar testing, only 23 of the 28 samples collected in June were submitted to the laboratory. These few filtered and preserved samples that were withheld generally represent "mid-range" dosages, or, in the case of the Bauxsol Proactive, a media that clearly performed poorly.

## Jar Test Results

Table 3 summarizes the analytical results (arsenic concentrations, pH, specific conductivity, Eh, and temperature) for the jar tests. The table is arranged such that results for the different media are grouped and presented in order of increasing media dosage. Results for concentrations of other analytes are attached to this memorandum.

Based on the initial arsenic concentration, the mass of media and water contained in each jar, and the final arsenic concentrations, the amount of arsenic adsorbed to the media can be calculated. These values are presented in Table 3 in milligrams arsenic adsorbed per gram media, and these values are the basis of determining the adsorption isotherm relationships between arsenic concentrations and the media being tested.

The five media with favorable arsenic adsorption results were Bayoxide E33, granular ferric hydroxide (GFH), Bauxsol Klosur (oxidant added), Dow Adsorbsia, and zero valent iron (ZVI). These media were carried forward in the calculation of adsorption isotherms as presented in the next section.

The other media tested (Taconite – all three types, Bauxsol Proactive, and unfumed slag) did not perform well. While these media did remove a slightly larger amount of arsenic than was seen with the clean silica sand control, large doses were required to see an effect. Therefore, these media were not carried forward in the analysis. Not surprisingly, the unfumed slag also leached some contaminants into the water such as barium, antimony, lead, zinc, nickel, and selenium (see attached data). Additionally, it is important to note that the Bauxsol Proactive (Bauxsol media without an oxidant added) did not perform well while the Bauxsol Klosur (with oxidant) did.



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The results of the manganese dioxide testing were mixed. The commercially available Erachem EMD manganese dioxide effectively oxidized arsenic, as well as adsorbing some of the arsenic. The Butte manganese dioxide slag did not have any effect on arsenic oxidation. Results from the mixture of the Erachem manganese dioxide and the taconite pellet fines did not indicate that oxidation of the arsenic improved adsorption onto the taconite media.

**Table 3**  
**Jar Test Results Summary**

Media	Sample ID	Media (g)	Water (g)	pH	SC (mS/cm)	Eh (mV)*	Arsenic Concentration (Cf, mg/L)**	Arsenic Speciation (mg/L)	delta As (mg/L)	mg As adsorbed	X/M (mg As/g media)
Original Groundwater (total recoverable)	PRBDH-17	NA	NA	7.18	2.43	121	40.6	As III = 37.0 As V = ND	—	—	—
None - oxidation test	PRBOX	NA	NA	7.51	2.16	395	38.16	--	—	—	—
Bayoxide	PRBBAY-2	0.51	1063.49	7.03	2.13	428	29	—	11.60	12.34	24.19
Bayoxide	PRBBAY-3	1.02	1065.98	7.04	2.13	379	20.96	—	19.64	20.94	20.53
Bayoxide	PRBBAY-4	5.02	1059.98	7.11	2.14	343	not submitted	--	—	—	—
Bayoxide	PRBBAY-5	10.09	1061.91	7.23	2.1	316	0.368	—	40.23	42.72	4.23
Bayoxide	PRBBAY-1	25	1051.9	7.6	2.09	224	0.099	—	40.50	42.60	1.70
GFH	PRBGFH-3	0.5	1067.5	7.02	2.13	311	25.12	—	15.48	16.52	33.05
GFH	PRBGFH-4	1.03	1064.97	6.99	2.13	300	14.62	—	25.98	27.67	26.86
GFH	PRBGFH-5	4.99	1060.01	6.98	2.13	317	not submitted	--	—	—	—
GFH	PRBGFH-2	10	1058	6.97	2.13	257	0.467	—	40.13	42.46	4.25
GFH	PRBGFH-1	25	1046	7.07	2.17	173	0.198	—	40.40	42.26	1.69
Bauxol Klosur (w/oxidant)	PRBKLO-3	0.51	1066.49	6.84	2.22	225	29.44	—	11.16	11.90	23.34
Bauxol Klosur (w/oxidant)	PRBKLO-2	1	1067.2	6.77	2.31	208	22.54	—	18.06	19.27	19.27
Bauxol Klosur (w/oxidant)	PRBKLO-4	3.1	1067.9	6.28	2.62	236	not submitted	--	—	—	—
Bauxol Klosur (w/oxidant)	PRBKLO-5	5.04	1063.96	6.08	2.98	206	0.822	—	39.78	42.32	8.40
Bauxol Klosur (w/oxidant)	PRBKLO-1	10	1060.9	5.93	4.06	179	0.592	—	40.01	42.44	4.24
ZVI	PRBZVI-3	25	1062	7.65	2.16	-66	21.86	—	18.74	19.90	0.796
ZVI	PRBZVI-4	50	1057	7.64	2.12	-63	7.43	—	33.17	35.06	0.701
ZVI	PRBZVI-2	101	1048.4	7.79	2.13	-71	2.83	—	37.77	39.60	0.392
ZVI	PRBZVI-1	400	997.2	9.08	2.13	-157	0.278	—	40.32	40.21	0.101
Unfumed Slag	PRBSLG-1	200	1011.1	7.75	2.2	15	31.94	—	8.66	8.76	0.044
Unfumed Slag	PRBSLG-2	400	956	8.43	2.22	77	15.62	—	24.98	23.88	0.060
Taconite tailings	PROTAI-1	300	963.4	7.23	2.22	211	27.2	—	13.40	12.91	0.043
Taconite concentrate	PRBTAC-2	51	1052	7.11	2.14	158	36.82	—	3.78	3.98	0.078
Taconite concentrate	PRBTAC-1	199	1008.8	7.22	2.18	184	28.38	--	12.22	12.33	0.062
Silica Sand	PRBSND-1	400	914.7	7.02	2.14	184	37.86	—	2.74	2.51	0.006

**Table 3**  
**Jar Test Results Summary**

Media	Sample ID	Media (g)	Water (g)	pH	SC (mS/cm)	Eh (mV)*	Arsenic Concentration (Cf, mg/L)**	Arsenic Speciation (mg/L)	delta As (mg/L)	mg As adsorbed	X/M (mg As/g media)
Bauxol Proactive (no oxid)	PRBPRO-1	20	1055.2	7.69	2.23	40	not submitted	--	--	--	--
Bauxol Proactive (no oxid)	PRBPRO-2	9.9	1062.2	7.48	2.22	62	not submitted	--	--	--	--
Original Groundwater, August (total recoverable)	DH-17-2	NA	NA	7.07	2.38	125	37.6	As III = 45.5 As V = ND	NA	NA	NA
Taconite pellet fines	PRBTCP-3	25	1046.5	7.47	2.12	396	35.6	--	2.00	2.09	0.08
Taconite pellet fines	PRBTCP-2	75.1	1036.6	7.95	2.17	390	35.4	--	2.20	2.28	0.03
Taconite pellet fines	PRBTCP-1	200.2	1012.7	8.24	2.21	383	31.1	--	6.50	6.58	0.03
Dow Adsorbsia	PRBDAD-3	1	1057.3	6.98	2.14	394	22.17	--	15.43	16.31	16.31
Dow Adsorbsia	PRBDAD-2	5.1	1034.1	6.61	2.35	414	4.03	As III = 4.96 As V = ND	33.57	34.71	6.81
Dow Adsorbsia	PRBDAD-1	20	1038.1	5.95	3.09	450	0.482	--	37.12	38.53	1.93
Butte MnO <sub>2</sub>	PRBBRW-2	20.1	1051.9	8.00	2.15	321	33.8	As III = 38.0 As V = ND	3.80	4.00	0.20
Butte MnO <sub>2</sub>	PRBBRW-1	67.3	1030.8	8.24	2.16	305	30.3	As III = 32.7 As V = ND	7.30	7.53	0.11
Erachem MnO <sub>2</sub> EMD	PRBEMD-2	6.1	1043.0	6.95	2.06	397	26.7	As III = 6.64 As V = 19.5	10.90	11.37	1.86
Erachem MnO <sub>2</sub> EMD	PRBEMD-1	24.9	1033.8	6.85	2.08	390	13.2	As III = 0.0484 As V = 12.2	24.40	25.23	1.01
Taconite + Erachem MnO <sub>2</sub>	PRBTEM-1	25g tac + 6.1g MnO <sub>2</sub>	1049.6	7.27	2.16	389	24.12	As III = 7.13 As V = 25.0	13.48	14.15	0.45

\*Eh adjusted relative to standard hydrogen electrode (SHE) by adding the direct mV reading to the relative potential of the Ag/AgCl electrode (calculated as 223.1 - 0.740(t), where t is in degrees Celsius)

\*\*Lab arsenic concentrations are filtered samples, with the exception of the total recoverable samples noted. Unfiltered groundwater was added to each jar at the beginning of testing.

## Adsorption Isotherms and Estimated Dosages

The Freundlich equation was used to construct adsorption isotherms for Bayoxide, GFH, Bauxsol Klosur, Dow Adsorbsia, and ZVI (Dobbs and Cohen, 1980). Data were fitted to the logarithmic form of the equation shown below:

$$\log(X/M) = \log K + (1/n)\log C_f$$

where:

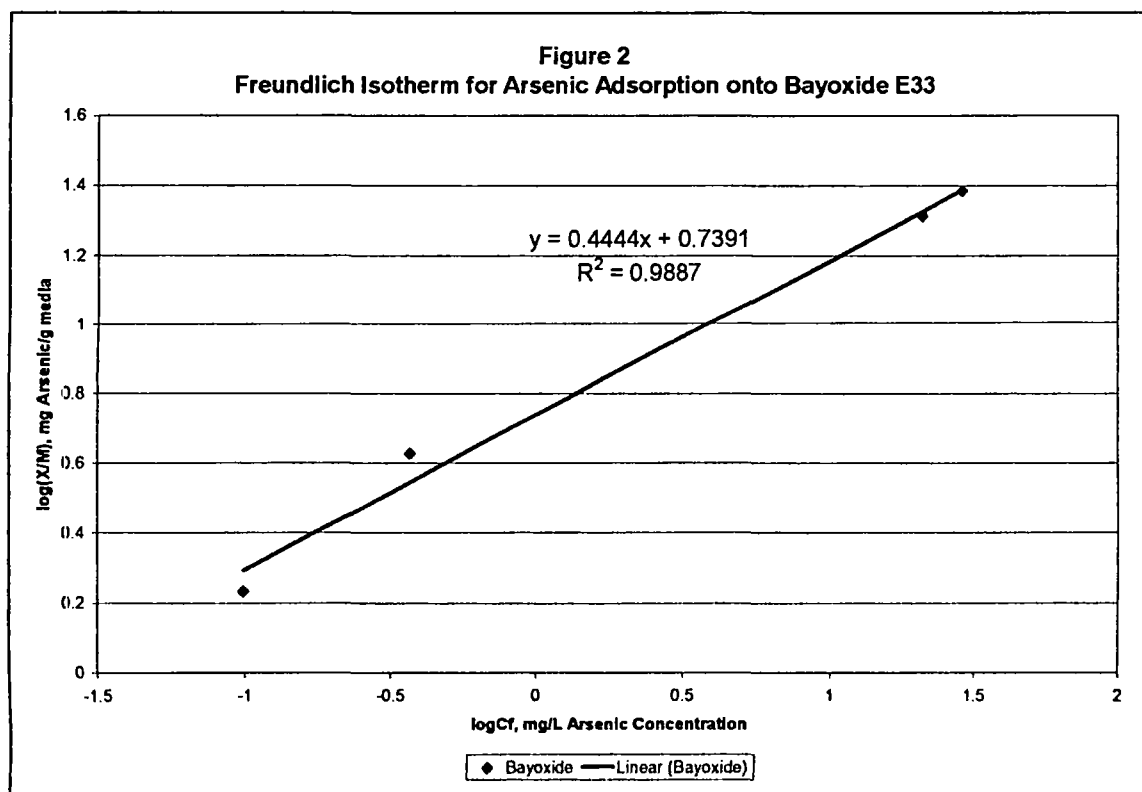
X = amount of arsenic adsorbed from a given volume of solution (initial minus final concentrations), milligrams

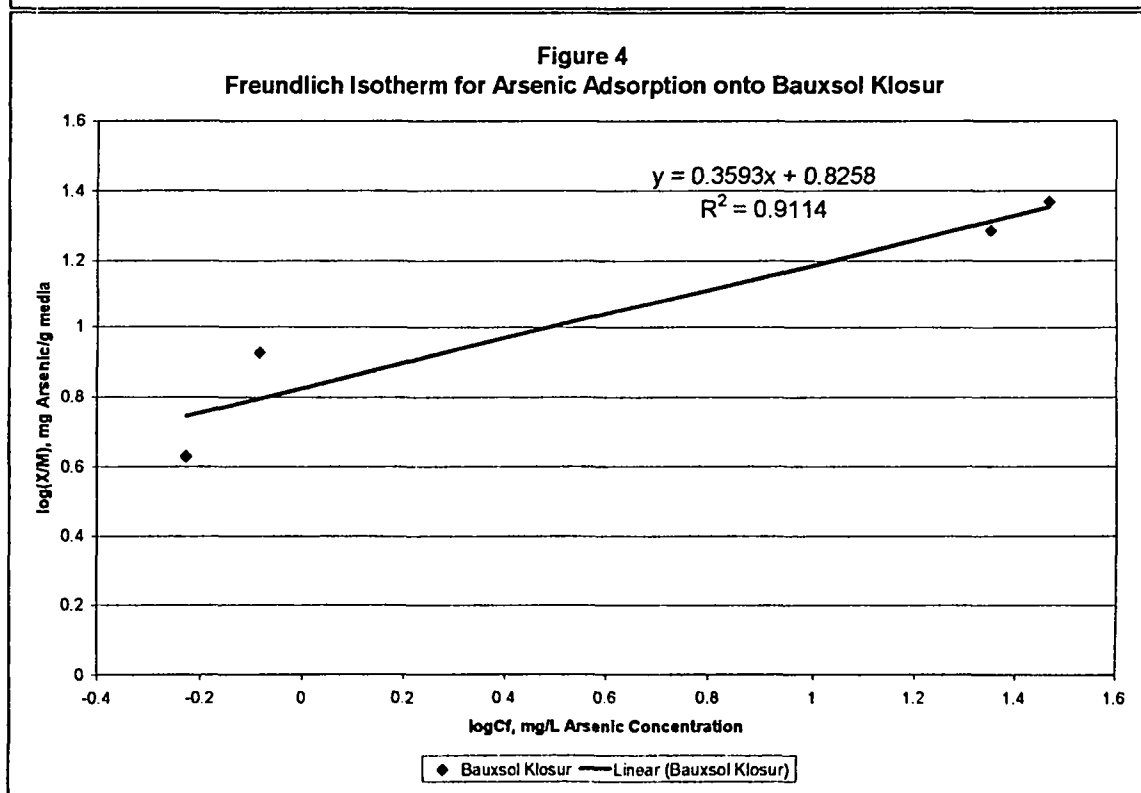
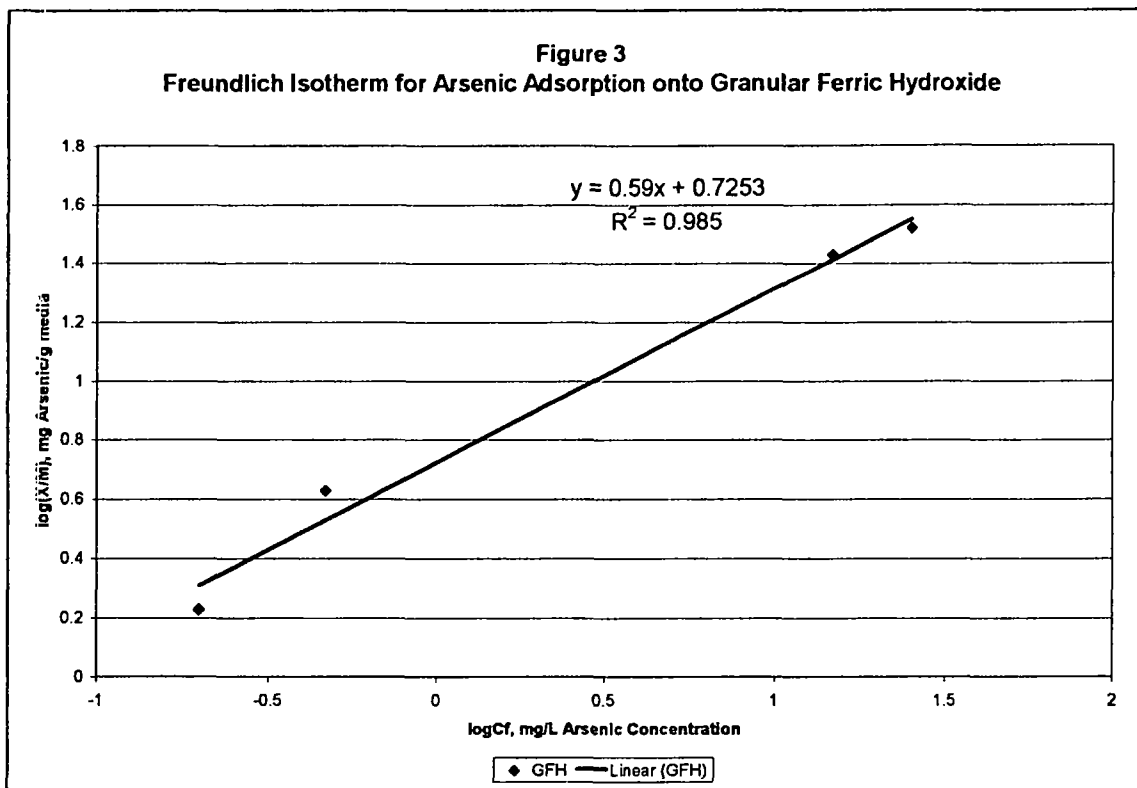
M = mass of media, grams

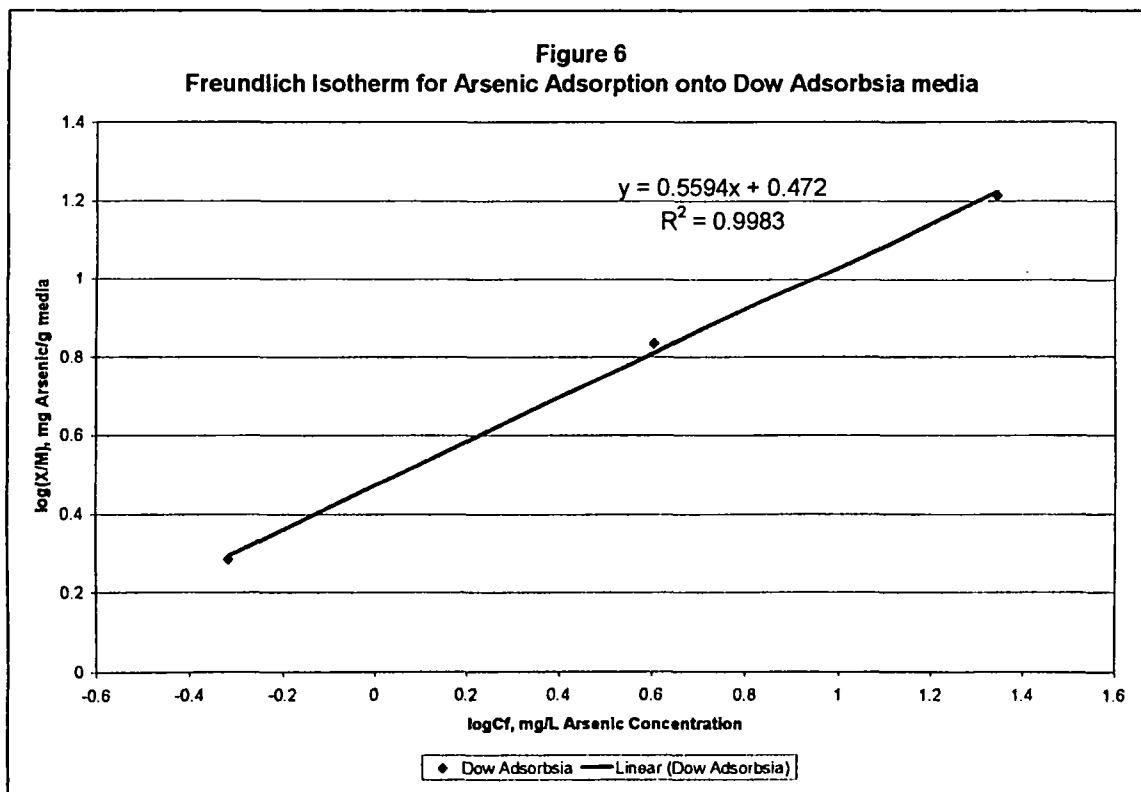
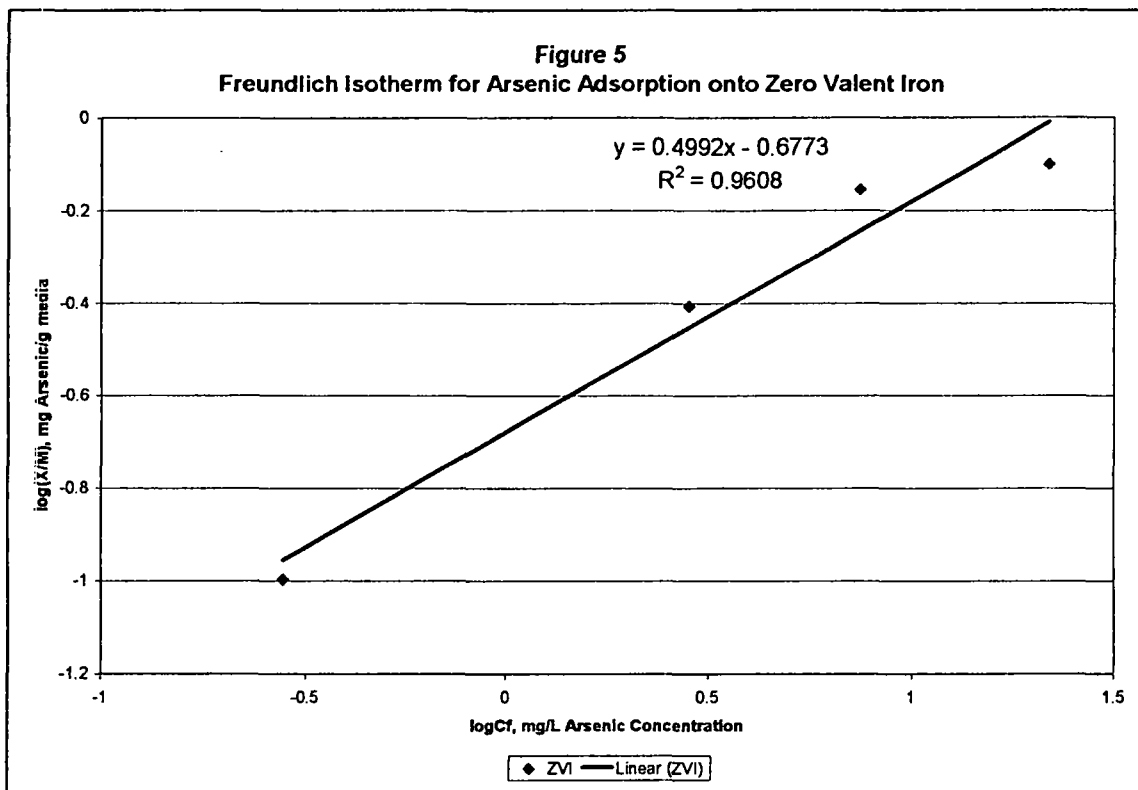
C<sub>f</sub> = equilibrium arsenic concentration remaining in the treated water, mg/L

K, n = empirical constants unique to the media and contaminant being tested.

Graphs of log(X/M) versus logC<sub>f</sub> are presented in Figures 2 through 6 for the different media. From the linear regression equation, logK was determined from the intercept and 1/n from the slope of the line.







Once K and n are determined from the experimental data, the Freundlich equation can be rearranged to solve directly for the mass of media required to achieve a desired concentration (in a single stage):

$$\log(C_o - C_f) - \log M = \log K + (1/n)\log C_f$$

where:

$C_o$  = initial arsenic concentration, mg/L

$C_f$  = targeted final arsenic concentration, mg/L

$M$  = mass of media required, g/L

This equation was used to determine the amount of media theoretically required to reduce the arsenic concentration from 40 mg/L down to the 0.01 mg/L (the MCL) in one stage (note: multiple stages are typically used in treatment systems because it results in a more efficient use of the media). Freundlich isotherm constants for the different media and calculated dosages required are summarized in Table 4.

**Table 4**

**Freundlich Adsorption Isotherm Constants and Estimated Media Dosages**

Media	logK (intercept)	K	1/n (slope)	$C_o$ (mg/L)	$C_f$ (mg/L)	logM	M = Media Dose required (grams media/liter)
Bayoxide	0.7391	5.4840	0.4444	40	0.01	1.75	56
GFH	0.7253	5.3125	0.5900	40	0.01	2.06	114
Bauxsol Klosur	0.8258	6.6958	0.3593	40	0.01	1.49	31
Dow Adsorbisia	0.472	2.9648	0.5594	40	0.01	2.25	177
ZVI	-0.6773	0.2102	0.4992	40	0.01	3.28	1,895

Freundlich isotherm constants for equation:  $\log(X/M) = \log K + 1/n(\log C_f)$

Media dosage to reduce concentration from 40 mg/L to 0.01 mg/L from equation:  $\log(C_o - C_f) - \log M = \log K + 1/n \log C_f$

The discussion of media dosages, while not directly applicable to the use of the media within a PRB, does provide a convenient measure of the performance of the media, allowing side by side comparisons to be made. The media with the lowest dosages (Bauxsol Klosur and Bayoxide) are the most efficient media. However, the results do not provide an indication of the life of the media (i.e. the adsorption capacity), which would be estimated using the Langmuir adsorption equation (see next section) and column studies (Phase II).

### Langmuir Isotherm Estimation of Capacities

The Langmuir equation was used to construct adsorption isotherms for Bayoxide, GFH, Bauxsol Klosur, Dow Adsorbisia, and ZVI in order to estimate capacities (EPA 1992). Data were fitted to the linearized form of the equation shown below:

$$C/(x/m) = 1/K_L M + C/M$$

where:

x = amount of arsenic adsorbed from a given volume of solution (initial minus final concentrations), milligrams

m = mass of media, kilograms

C = equilibrium arsenic concentration remaining in the treated water, mg/L

$K_L$  = empirical Langmuir constant unique to the media and contaminant being tested, L/mg

M = empirical constant, considered the adsorption maximum or maximum concentration that the adsorbent can retain, mg/kg.

Graphs of  $C/(x/m)$  versus C were generated for the different media. From the linear regression equation,  $1/K_L M$  was determined from the intercept and  $1/M$  from the slope of the line. The capacities (M) for the different media are summarized in Table 5.

**Table 5**

**Langmuir Isotherm Constants and Estimated Maximum Capacities**

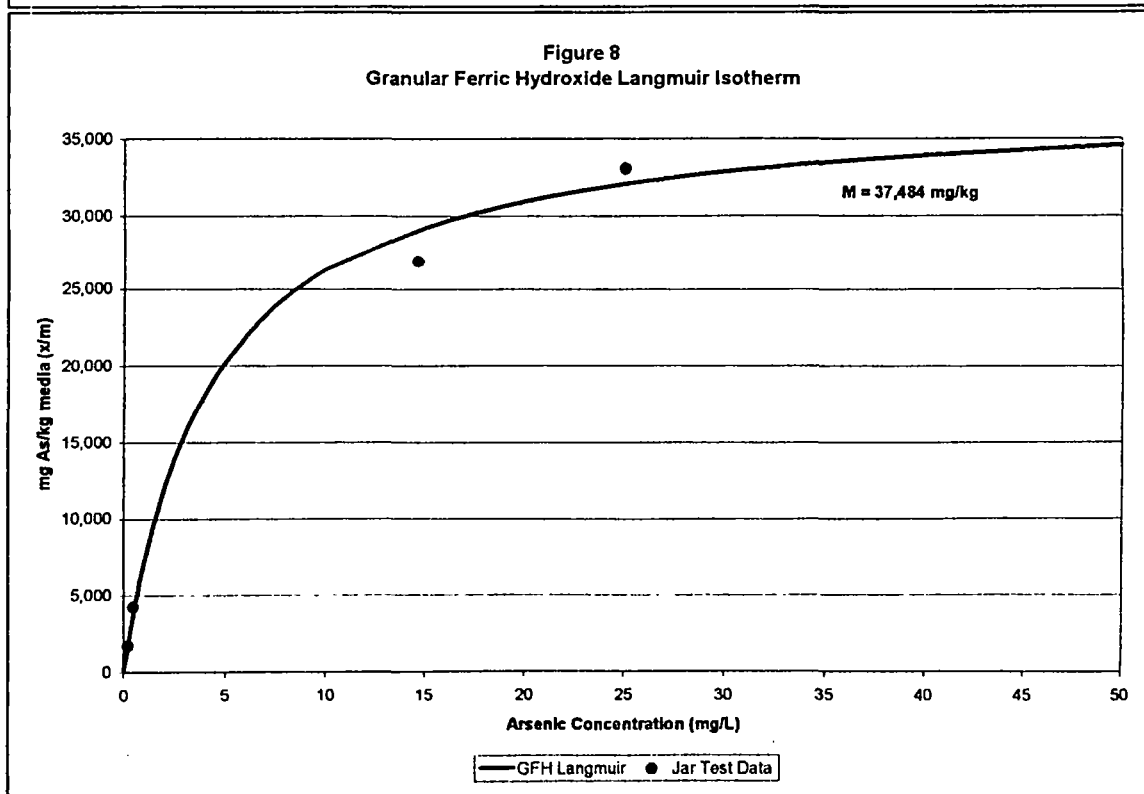
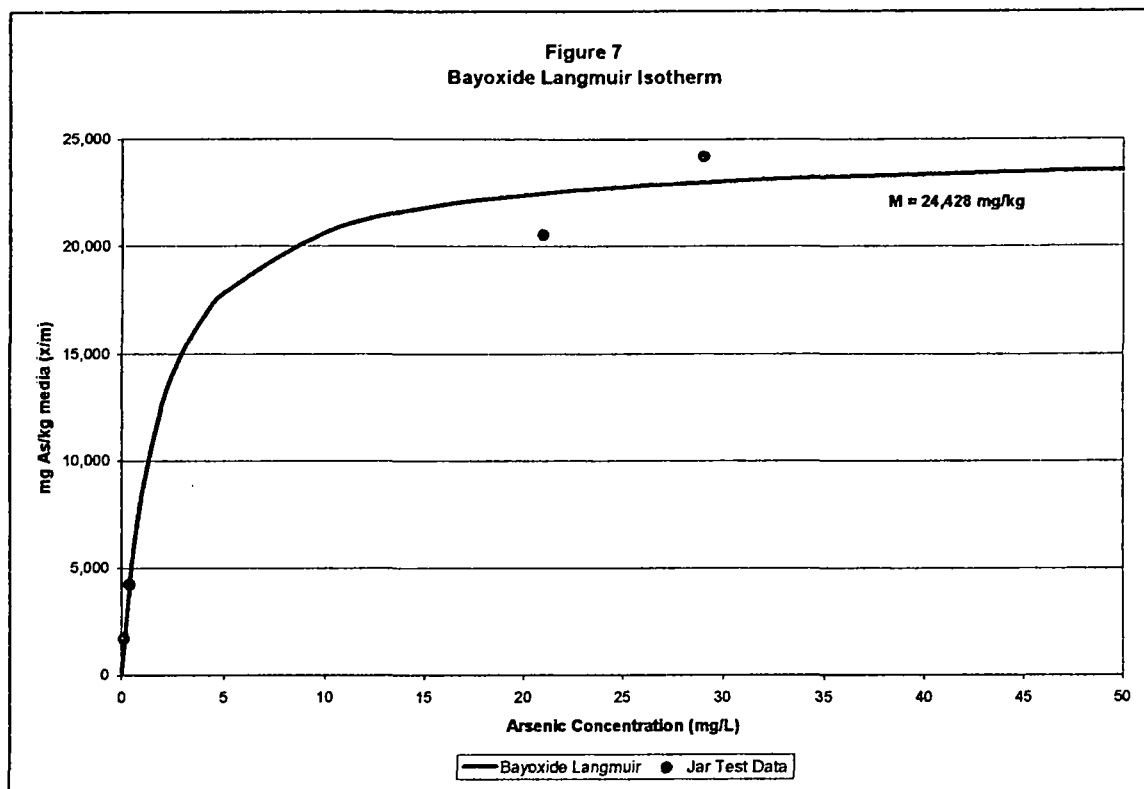
Media	$1/K_L M$ (intercept)	$K_L$	$1/M$ (slope)	M (mg As/kg media)
Bayoxide	7.520 E-5	0.544	4.094 E-5	24,428
GFH	1.134 E-4	0.235	2.668 E-5	37,484
Bauxsol Klosur	1.025 E-4	0.413	4.229 E-5	23,644
Dow Adsorbisia	3.047 E-4	0.158	4.824 E-5	20,731
ZVI	2.970 E-3	0.376	1.116 E-3	896

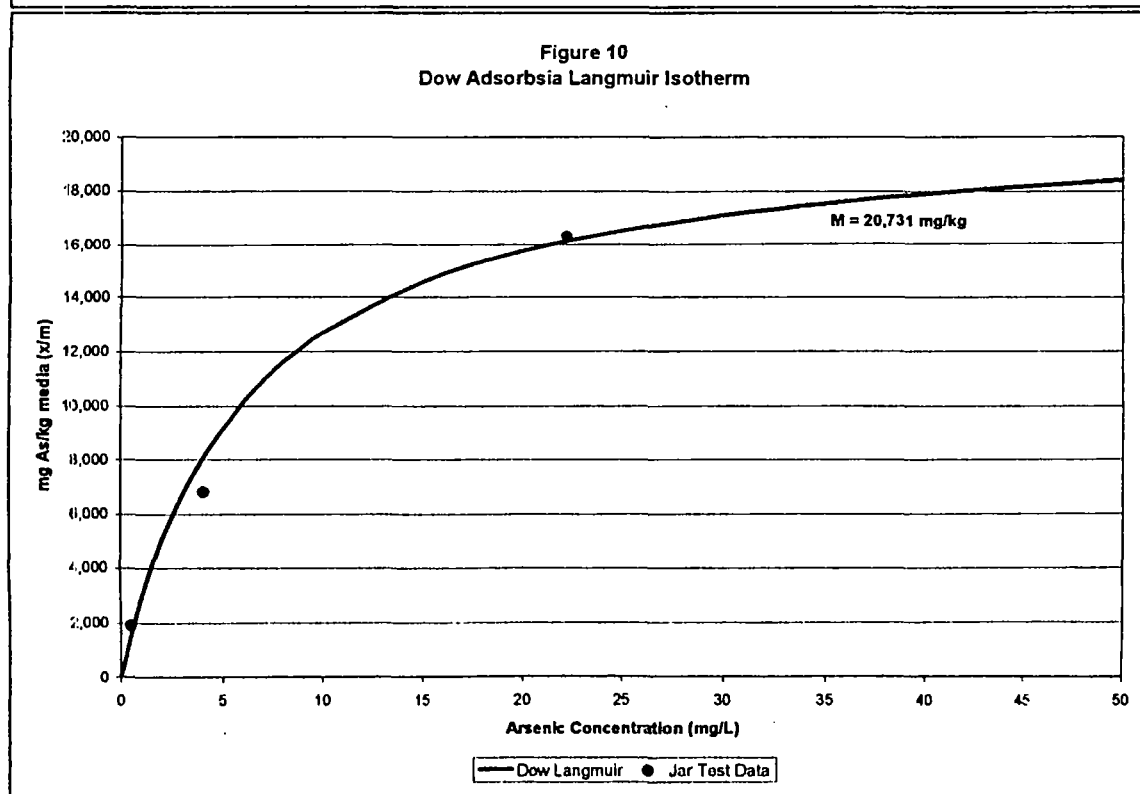
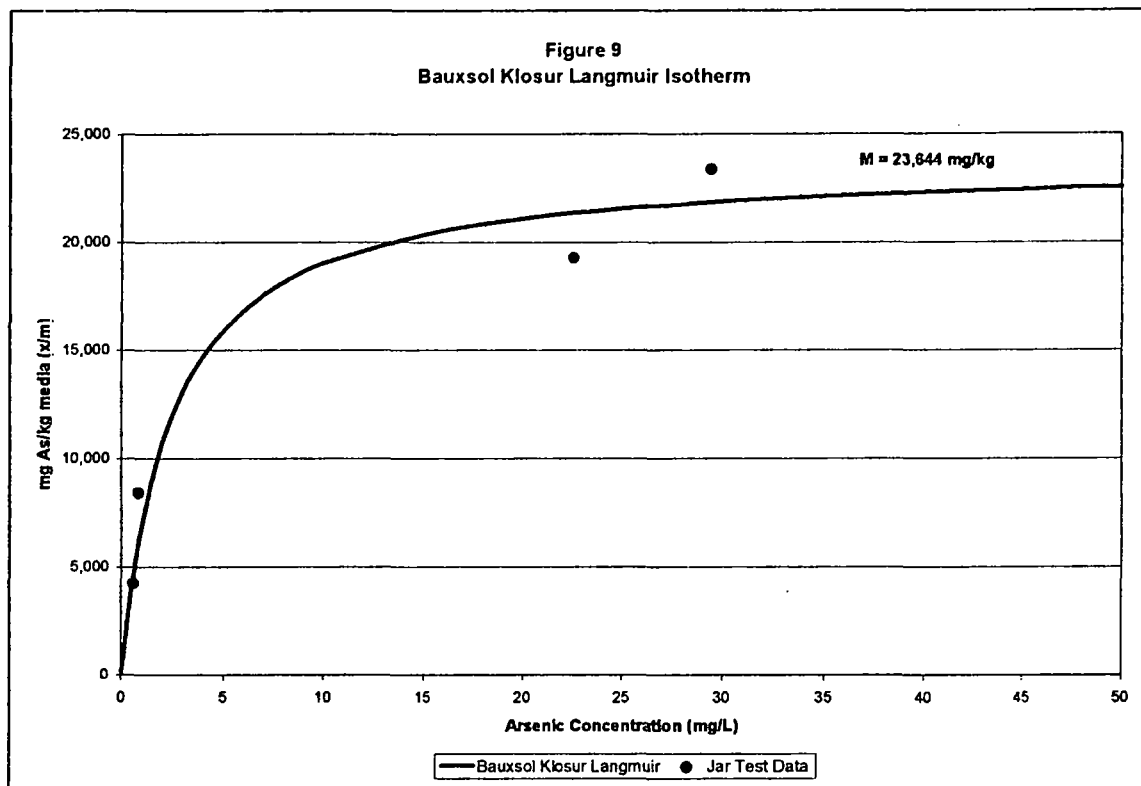
With derivation of the Langmuir constants, non-linearized isotherms were generated to visually show the adsorption maxima for each of the media according to the equation:

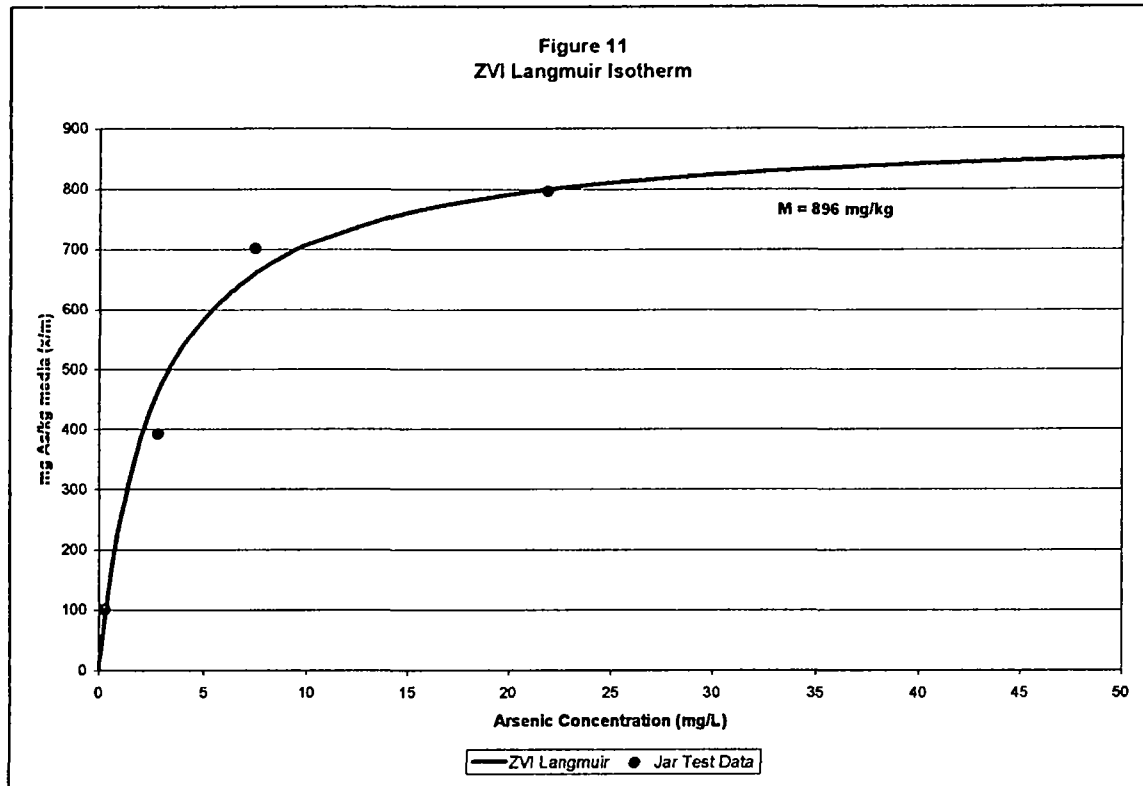
$$x/m = K_L M C / (1 + K_L C)$$

These are shown in Figures 7 through 11. Based on these calculations, the GFH media has the highest adsorption capacity. Additionally, the apparent low capacity of the ZVI is misleading because the capacity should be higher as the media undergoes oxidation.









## Media-Related Issues

In further discussion with the media vendors, issues outside of arsenic removal performance became apparent that would limit the applicability of several of these media in a full-scale PRB wall.

For the Bauxsol Klosur, two issues were apparent. First, the media was in a powdered form, which would not be suitable in construction of a permeable wall. Discussion with Virotech, the vendor, indicated that their bauxsol products had been used primarily in slurry injections for source control applications. However, the bauxsol had not been used in a permeable wall. They were working on a pelletized form of the product that might be suitable in a PRB setting, but did not have a product available yet. Second, arsenic removal was dependent on oxidation of the arsenic (i.e., the Bauxsol Proactive did not remove arsenic), and hence, the presence of the oxidant added. Virotech was uncertain about the longevity of the oxidant and agreed that the mode of failure in a PRB setting would be premature depletion of the oxidant before the adsorptive capacity of the media was filled. Given these uncertainties, the Bauxsol products were not carried forward in the cost analysis.

For the GFH, the potential volume of media that would be required in a full-scale wall became a limiting issue. In obtaining media costs from the vendors, a rough estimate was

made on the volume of media that would be required for a full-scale PRB wall. The ballpark estimate assumed a 2-foot wide trench, 30 feet deep and 500 feet across, or about 30,000 cubic feet (roughly 1,200 cubic yards). Siemens (GFH vendor) indicated that it would be impossible for them to produce enough media to meet those volume requirements (they would require 18 months to two years to produce that volume). Thus, even though the GFH media performed well in the arsenic adsorption testing, the vendor may not be able to provide the volume of media required.

The Bayoxide E33 media is still a potential candidate for consideration. However, the material itself, while granular, is lightweight and may collapse or compact significantly under its own weight in a full-scale setting. Additionally, until the material is wetted, the Bayoxide initially floats, which would make construction of a wall below the groundwater table problematic.

The Dow Adsorbsia media appeared to physically disintegrate during the overnight tumbling, indicating that it too may collapse under its own weight in a full-scale setting. The water decanted from the media was milky white with fines and was difficult to filter. Additionally, the media had clumped and adhered to the sides of the jars. If the media broke down into a finer size fraction during the tumbling, this would have increased the surface area available for adsorption, and may have artificially increased the apparent adsorption efficiency of the media.

### Media Costs Relative to Required Dosage

Using the media dosages calculated above and the costs of the media, unit treatment costs were estimated to allow comparisons among the different media.

Table 6 compares the media dosages, densities, and unit costs of the Bayoxide, GFH, Dow Adsorbsia, and ZVI media that were used to derive unit treatment costs (dollars per thousand gallons treated).

**Table 6**  
**Comparison of Estimated Treatment Costs**

Media	Langmuir Isotherm Maximum Capacity* (mg As/kg media)	Freundlich Isotherm Calculated Required Dose** (g media/L water)	Media Required (lbs/kgal)	Bulk Density (lbs/cf)	Media Unit Cost (\$/cf)	Treatment Cost per thousand gallons (\$/kgal)
Bayoxide	24,428	56	471	29	\$150.00	\$2,434
GFH	37,484	114	950	72	\$205.00	\$2,704
Dow Adsorbsia	20,731	177	1,476	44	\$400.00	\$13,415
ZVI	896	1,895	15,800	150	\$37.50***	\$3,950

\* From Table 5

\*\*From Table 4, assumes 40mg/L concentration treated to 0.01mg/L in one stage

\*\*\*ZVI cost from Peerless metals

Media costs do not include freight costs

Clearly, the Dow Adsorbisia media is cost prohibitive at roughly 3-5 times the unit cost of the other materials. This comparison shows that even though the Bayoxide E33 and GFH are more expensive materials by weight, the higher efficiencies and capacities require less material, and the unit treatment cost is theoretically lower than the ZVI. However, these results would need to be verified using column testing. Further, as discussed in the previous section, even though these materials were effective chemically, there are implementability issues with the Bayoxide and GFH that could limit their use in a full-scale PRB wall.

## References

Dobbs, Richard A. and Jesse M. Cohen. 1980. Carbon Adsorption Isotherms for Toxic Organics. Wastewater Research Division, Municipal Environmental Research Laboratory, Cincinnati, Ohio. U.S. Environmental Protection Agency document EPA-600/8-80-023. April 1980.

EPA 1992. Batch-Type Procedures for Estimating Soil Adsorption of Chemicals. U.S. Environmental Protection Agency Technical Resource Document EPA/530/SW-87/006-F. April 1992.

Additional Analytical Results  
East Helena PRB Jar Testing - 2007  
(all results mg/L)

Sample ID	PRBDH-17		PRBOX	PRBZVI-1	PRBZVI-2	PRBZVI-3	PRBZVI-4	PRBGFH-1	PRBGFH-2	PRBGFH-3	PRBGFH-4	PRBBAY-1	PRBBAY-2	PRBBAY-3	PRBBAY-5	PRBKLO-1	PRBKLO-2	PRBKLO-3	PRBKLO-5
	Dissolved	Total	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved
Aluminum	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.5	0.4	0.2	1.1
Antimony	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U
Arsenic	36.84	40.6	38.16	0.278	2.83	21.86	7.43	0.198	0.467	25.12	14.62	0.099	29	20.96	0.368	0.592	22.54	29.44	0.522
Barium	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U
Beryllium	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U
Cadmium	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U
Calcium	29	30	30	19	27	30	29	8	16	29	27	19	30	30	28	60	29	29	37
Chromium	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U
Cobalt	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U
Copper	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U
Iron	0.57	0.63	0.14	0.11	15.66	29.98	23.94	0.03 U	0.03 U	0.03 U	0.03 U	0.03 U	0.03 U	0.03 U	0.04	0.03 U	14.98	0.19	0.21
Lead	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U
Magnesium	9	9	9	6	9	9	9	6	8	9	9	2	9	9	6	14	9	9	10
Manganese	1.39	1.43	1.43	0.17	1.78	1.94	1.95	0.11	0.28	1.16	0.93	0.28	0.96	0.66	0.04	1.39	1.21	1.24	1.32
Mercury	0.001	0.001 U	0.001	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U
Nickel	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U
Potassium	10	11	11	11	11	11	11	10	10	11	11	11	11	10	11	13	10	11	11
Selenium	0.005 U	0.005 U	0.012	0.011	0.011	0.011	0.011	0.011	0.012	0.013	0.013	0.012	0.012	0.012	0.013	0.012	0.012	0.012	0.013
Silica	14.7	15.7	15.4	3.3	7.1	16.5	11.5	1	2.6	13.9	11.7	0.6	14.8	13.9	0.8	95.5	19.9	16.1	62.5
Silver	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U
Sodium	580	621	601	598	602	601	600	591	600	604	598	615	608	605	610	1210	653	628	662
Thallium	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U
Tin	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U
Vanadium	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U
Zinc	0.17	0.17	0.12	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01	0.03	0.02	0.01	0.03	0.02	0.01 U	0.09	0.04	0.04	0.07

Additional Analytical Results  
East Helena PRB Jar Testing - 2007  
(all results mg/L)

Sample ID	PRBSND-1 Dissolved	PRBTAL-1 Dissolved	PRBSLG-1 Dissolved	PRBSLG-2 Dissolved	PRBTAC-1 Dissolved	PRBTAC-2 Dissolved	DM-17-2 (August 26, 2007)		PRBTCP-1 Dissolved	PRBTCP-2 Dissolved	PRBTCP-3 Dissolved	PRBDAD-1 Dissolved	PRBDAD-2 Dissolved	PRBDAD-3 Dissolved	PRBBRW-1 Dissolved	PRBBRW-2 Dissolved	PRBEMD-1 Dissolved	PRBEMD-2 Dissolved	PRBEM-1 Dissolved
Aluminum	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Antimony	0.005 U	0.005 U	0.104	0.174	0.005 U	0.005 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Arsenic	37.86	27.2	31.94	15.62	28.38	36.82	37.9	37.6	31.1	35.4	35.6	0.482	4.03	22.17	30.3	33.8	13.2	26.7	24.12
Barium	0.1 U	0.1 U	0.1	0.1	0.1 U	0.1 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Beryllium	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Cadmium	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	0.001 U	-	-	-	-	-	-	-	-	0.001 U	0.001 U	-	-	-
Calcium	31	40	40	53	38	32	-	-	-	-	-	-	-	-	-	-	-	-	-
Chromium	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Cobalt	0.01 U	0.01 U	0.02	0.01 U	0.01 U	0.01 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Copper	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U	-	-	-	-	-	-	-	-	0.01	0.01	-	-	-
Iron	0.03	0.18	3.46	0.18	0.37	0.36	-	-	-	-	-	-	-	-	0.03 U	0.03 U	-	-	0.03
Lead	0.01 U	0.01 U	0.19	0.19	0.01 U	0.01 U	-	-	-	-	-	-	-	-	0.01 U	0.01 U	-	-	-
Magnesium	9	18	10	11	14	10	-	-	-	-	-	-	-	-	-	-	-	-	-
Manganese	1.39	0.73	2.48	1.7	0.98	1.28	-	-	-	-	-	-	-	-	10.88	17.22	0.3	1.55	0.72
Mercury	0.001 U	0.001 U	0.001	0.001	0.001 U	0.001 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Nickel	0.01 U	0.01 U	0.03	0.03	0.01 U	0.01 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Potassium	11	45	20	22	32	19	-	-	-	-	-	-	-	-	-	-	-	-	-
Selenium	0.011	0.012	0.017	0.035	0.012	0.013	-	-	-	-	-	-	-	-	-	-	-	-	-
Silica	17.4	21.9	22.4	28.2	20	16.7	-	-	-	-	-	-	-	-	-	-	-	-	-
Silver	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Sodium	607	588	613	617	588	597	-	-	-	-	-	-	-	-	-	-	-	-	-
Thallium	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	0.005 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Tin	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Vanadium	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	-	-	-	-	-	-	-	-	-	-	-	-	-
Zinc	0.06	0.01 U	0.81	0.05	0.02	0.03	-	-	-	-	-	-	-	-	0.01 U	0.02	-	-	-